

# EFFECTS OF COAL STRUCTURE AND PROCESSING CONDITIONS ON ORGANIC EFFLUENTS FROM SLAGGING FIXED-BED GASIFICATION

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## INTRODUCTION

Slagging fixed-bed gasification of low-rank coals is being investigated at the Grand Forks Energy Technology Center. In support of environmental and waste treatment studies, research is underway to determine the effect of process parameters on effluent production and composition.

The GFETC gasifier is a 1 ton/hour, pilot plant unit. The coal feed moves slowly down a shaft and is reacted with an oxygen-steam mixture injected through four tuyeres into the hearth. The product gas exits the gasifier at the top of the shaft. Operating parameters that may vary from test to test are pressure, 100 to 400 psig; oxygen/ steam molar ratio, 0.9 to 1.1; and oxygen feed rate, 4000 to 6000 scfh. Detailed information on the GFETC pilot plant studies has been published previously (1-3).

Tar, oils, water vapor and coal particles are removed from the exiting raw gas stream in a spray washer. The liquids that accumulate in the spray washer are sampled periodically. A recent publication (4) describes spray washer sampling procedures. Samples considered in this report were collected at the end of the test.

An inherent problem in the analysis of effluents from coal conversion processes is the complexity of the mixtures. Several schemes have been suggested for the analysis and environmental assessment of coal gasification effluents. The methodology defined by the EPA-IERL/RTP Procedure Manual: Level 1 Environmental Assessment (5) was applied to the analysis of spraywasher samples. Effluent samples produced by gasification of three coals at a range of conditions were used for this study.

## EXPERIMENTAL

Figure 1 is the flow diagram of the separations and analyses performed on the tar and liquor samples.

Simulated distillation was obtained by FID gas chromatography using 3% OV-17, 1/8" x 4' ss columns. The temperature was programmed from 50 to 300°C at 10°/min. ASTM standard D2887 was used to establish boiling point ranges. The extracted organics were separated using gradient elution liquid chromatography. Silica gel adsorbent was used. Table 1 shows the solvent sequence for the procedure.

FIGURE 1. Analytical Flow Diagram for Spraywasher Tar and Liquor

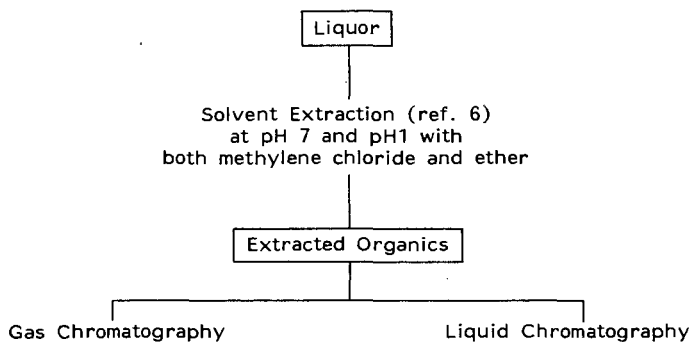
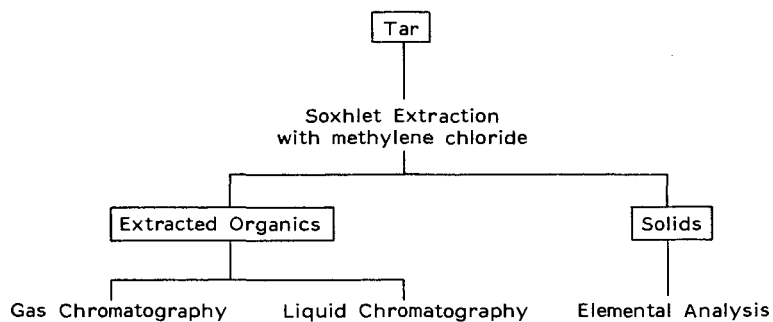


TABLE 1. Solvent Series for LC Separations

<u>Fraction</u>	<u>Solvent Composition</u>
1	Pentane
2	20% methylene chloride in pentane
3	50% methylene chloride in pentane
4	Methylene chloride
5	5% methanol in methylene chloride
6	20% methanol in methylene chloride
7	50% methanol in methylene chloride
8	Methanol

Instruments used in this study were an AEI MS-30\* mass spectrometer, Perkin-Elmer 240 elemental analyzer, Leco sulfur analyzer, Varian 2400 gas chromatograph, and Perkin-Elmer 283 infrared spectrophotometer.

## RESULTS

End-of-run tar and liquor samples produced from five gasification tests were obtained for this study. The summary of coals and operating parameters for these tests is shown in Table 2.

TABLE 2. Summary of Coals and Operating Parameters

<u>Run No.</u>	<u>Coal/Rank</u>	<u>Operating Pressure (psig)</u>	<u>Oxygen Feed Rate (scfh)</u>	<u>Oxygen-Steam Molar Ratio</u>
RA-40	Indian Head Lignite	200	4000	1.0
RA-52	Indian Head Lignite	300	6000	1.0
RA-37	Indian Head Lignite	400	6000	1.0
RA-45	Rosebud Subbituminous	200	4000	1.1
RA-58	Gascoyne Lignite	300	6000	1.1

Tar

The as-received tar contained 28 to 35% extractable organic material, 0.4 to 2.0% solids (entrained coal particles) and 63 to 71% water. The gas chromatographic analysis of the organic extracts is shown in Table 3.

TABLE 3. GC Analysis of Organics Extracted from Tar

<u>Range</u>	<u>BP(°C)</u>	<u>% of Extract</u>				
		<u>RA-40</u>	<u>RA-52</u>	<u>RA-37</u>	<u>RA-45</u>	<u>RA-58</u>
C <sub>7</sub>	90 to 110	0.4	0.1	0	0	1.5
C <sub>8</sub>	110 to 140	0.8	0.2	0.1	0	2.4
C <sub>9</sub>	140 to 160	0.1	0.6	0.2	0.2	3.3
C <sub>10</sub>	160 to 180	1.1	0.6	0.3	0.8	6.8
C <sub>11</sub>	180 to 200	2.5	0.8	0.6	1.4	5.0
C <sub>12</sub>	200 to 220	10.0	11.6	11.8	7.3	20.0
>C <sub>12</sub>	> 220	85.1	86.1	87.0	90.3	61.0

\* Identification of specific brands or models is done to facilitate understanding and does not constitute or imply endorsement by the Department of Energy.

The distribution of compound classes in the liquid chromatography separations was determined by low voltage mass spectrometry and confirmed by infrared spectroscopy. Fraction 1 consists of paraffins and olefins, mostly branched. Fractions 2 and 3 consist primarily of naphthalene, C<sub>1</sub> and C<sub>2</sub> naphthalenes, and C<sub>1</sub> biphenyl or C<sub>1</sub> acenaphthene. Fractions 4 and 5 consist primarily of C<sub>1</sub> acenaphthylene or C<sub>1</sub> fluorene, phenanthrene, anthracene, C<sub>1</sub> and C<sub>2</sub> phenanthrene, C<sub>1</sub> and C<sub>2</sub> anthracene, fluoranthene, pyrene, and C<sub>1</sub> pyrene. Fractions 6 and 7 consist primarily of C<sub>1</sub> and C<sub>3</sub> indoles, naphthol, C<sub>1</sub> and C<sub>2</sub> naphthols, carbazole, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> pyridines, phenol, and C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> phenols. No specific assignments were made to the compounds in fraction 8. The results of the liquid chromatography separations of the organics extracted from the tar are shown in Table 4.

TABLE 4. LC Analysis of Organics Extracted from Tar

Fraction(s)	% of Extract				
	RA-40	RA-52	RA-37	RA-45	RA-58
1	10.3	11.4	9.0	12.0	13.0
2,3,4	32.3	29.9	27.8	33.9	41.0
5,6,7	51.8	57.4	61.7	48.6	45.3
8	5.6	1.3	1.5	5.5	0.7

#### Liquor

Runs RA-40, RA-45, and RA-58 liquor yielded from 1200 to 2050 ppm solvent extractable organics. It is unlikely that the majority of organics were extracted since the total organic carbon for these liquors ranges from 6550 to 7800 ppm. The gas chromatography analysis of the extracted organics is shown in Table 5.

TABLE 5. GC Analysis of Organics Extracted from Liquor

Range	BP(°C)	% of Extract		
		RA-40	RA-45	RA-58
C <sub>7</sub>	90 to 110	0	0	0.4
C <sub>8</sub>	110 to 140	0	0	0.7
C <sub>9</sub>	140 to 160	0	0	1.3
C <sub>10</sub>	160 to 180	0	0	2.5
C <sub>11</sub>	180 to 200	0.1	0	3.2
C <sub>12</sub>	200 to 220	16.1	11.5	7.8
>C <sub>12</sub>	> 220	83.9	88.5	84.0

The liquid chromatography separations of the organic extract were not useful in defining specific classes of compounds. There was a considerable amount of overlap in the compounds found in fractions 5 through 8. These fractions consist primarily of C<sub>4</sub> and C<sub>5</sub> benzenes, C<sub>1</sub> and C<sub>2</sub> pyridines, C<sub>2</sub> and C<sub>3</sub> phenols, quinolines, naphthols, phenanthrene, anthracene, binaphthyl, and thiophenes. These assignments were made by mass spectrometry and infrared spectroscopy. The liquid chromatography analysis of the extracted organics is shown in Table 6.

TABLE 6. LC Analysis of Organics Extracted from Liquor

Fraction(s)	% of Extract		
	RA-40	RA-45	RA-58
1	0	0	1.6
2,3,4	0.4	0.4	8.3
5,6,7	80.8	89.2	83.0
8	18.8	10.2	7.1

#### Tar Solids

The solids were found to contain a higher percentage of mineral matter than the original coal feed. The relative proportion of nitrogen and sulfur was also higher in the solids. For RA-45, the coal feed contained 0.85% nitrogen and 1.81% sulfur; the solids contained 3.32% nitrogen and 2.42% sulfur. Table 7 shows the ultimate analyses of the tar solids and the feed coals.

TABLE 7. Comparison of Tar Solids with Feed Coal

	RA-40		RA-45		RA-58	
	feed coal	tar solids	feed coal	tar solids	feed coal	tar solids
Ultimate Analysis*, pct						
C	64.42	65.34	64.23	58.99	62.14	63.05
H	4.35	4.11	4.31	1.49	4.39	3.05
N	0.85	3.32	1.01	1.46	0.84	1.21
S	1.81	2.42	2.05	3.59	1.42	1.74
O(by diff)	18.23	13.77	13.06	0.66	18.06	10.22
Ash	10.34	11.04	15.34	33.81	13.15	20.73

\*moisture-free basis

## DISCUSSION

### Tar Characterization

The variation observed in the amount of organic material extracted from the tar phase is consistent with experimental error in sampling. The procedure for obtaining tar samples has been described previously (4). The phase separation of tar from liquor depends on operator judgement in observing the interface between two darkly colored phases. Tar extraction data for runs 40, 45, and 58 shows a relative standard deviation of 6.01% for the amount of water. Three other runs made with Indian Head lignite at 200 psi and 4000 scfh oxygen rate showed a relative standard deviation of 6.47% for water content. Thus the variation between samples of different coals tested at different gasification conditions is nearly identical to that for replicate runs with the same coal.

The boiling point distribution of the tar extract shows distinct differences when comparing tars obtained from different coals gasified under same conditions. For example, a comparison of Rosebud and Indian Head gasified at 200 psi shows the tar from Indian Head to be comprised of more lower boiling materials. The cumulative boiling point distribution shows that 46% of Indian Head tar has distilled by 254°C and 87% by 343°, while the comparable figures for Rosebud tar are 34% and 76%. Of these two coals, Indian Head contains the greater amount of volatile

matter on an maf basis. A similar effect was observed for tars from gasification of Gascoyne and Indian Head lignites at 300 psi: Gascoyne contains a greater amount of volatile matter and produces more low boiling compounds in the tar.

A comparison of the boiling point distributions of tars produced from gasification of Indian Head lignite at different pressures shows that the effect of increasing gasification pressure is to shift the boiling point distribution downward. For example, the temperatures at which 75% of the tar has distilled drop from 316°C for tar produced at 200 psi, to 287° for 300 psi, and to 271° for tar produced at 400 psi. The fraction corresponding to phenol (180-200°C) decreases with increasing gasification pressure, as shown previously (7) for a high-pressure, low-temperature carbonization process in the SFBG.

The amounts of the fractions obtained in the liquid chromatographic separations of the tar were correlated with gasification conditions and coal composition. The treatment used followed the fractional factorial analysis procedures given by Lipson and Sheth (8). Since the absolute numerical values of the factors vary over several orders of magnitude -from thousands of scfm for oxygen feed rates to one or two percentage units for coal nitrogen and sulfur - comparisons were made on the basis of percentage changes in each factor.

The amounts of fractions 1 (paraffins and olefins), 2-4 (aromatics), and 5-7 (polar compounds) depend most heavily on the maf carbon content of the coals. Both the paraffins and olefins and the aromatics show a direct correlation with maf carbon, while the polar compounds vary inversely. These results demonstrate that as more carbon is added to the molecular framework of the coal proportionately fewer oxygen or nitrogen functional groups will be present; hence as the coal undergoes pyrolysis or hydrocracking in the carbonization zone of the SFBG (9) relatively fewer polar species will be formed. Correlation of the amounts of one LC fraction vs. another show that the paraffins and olefins are directly proportional to the aromatics, but that both the paraffin-olefin and the aromatic fractions vary inversely with the polar fraction.

When the effect of maf carbon content in the coal is removed statistically (8), no other factors were found to influence the amount of the paraffin-olefin fraction. The amount of the aromatic fraction, corrected for the effect of carbon, shows a direct correlation with the amount of hydrogen in the product gas. A recent publication (10) describing the detailed mass spectroscopic analysis of SFBG tars also demonstrated such a correlation for the concentrations of many of the aromatic compounds. The amount of the polar fraction showed no other correlations above the 80% confidence limit.

With respect to the amount of the very polar fraction (fraction 8) no factors were found to display both a large slope and greater than 80% confidence correlation.

#### Liquor Characterization

The amount of organic material extractable from the liquor accounted for only 18 to 28% of the total organic carbon content of the samples. The amount of extractable material shows an inverse correlation with the maf oxygen content of the coal. As the oxygen content of the coal increases, more compounds with polar functional groups should appear in the organic effluents; these compounds should dissolve in the liquor and in turn be resistant to extraction into relatively non-polar solvents. The amount of extractable organic material when added to the "phenols" as determined by gas chromatographic analysis of filtered liquor (11) agrees well with the total organic carbon content. For example, in the liquor produced during gasification of Rosebud coal, phenols accounted for 75.9% of the TOC and the extractable organics, 28.3%.

The boiling point distributions of liquor organic extracts from gasification of Indian Head (RA-40), Rosebud, and Gascoyne are similar. The most appreciable difference is that the extract from liquor produced in gasification of Gascoyne lignite is the only one of the three samples containing material boiling below 196°C. The liquid chromatographic separation of the extract from Gascoyne liquor was the only one showing material in the paraffin-olefin and aromatic fractions.

A correlation of the amounts of fractions in the liquid chromatographic separations with gasification conditions and coal composition was performed in the same manner as for the tar extracts. Only the polar and polar fractions were considered, and only the three samples from runs 40, 45, and 58 were used.

The major factor affecting the amount of both fractions is the maf carbon content of the coal. The polar fraction correlates directly with maf carbon; the very polar fraction thus shows an inverse correlation, since these two fractions account for 90 to 99% of the total material in the liquor or organic extract.

#### Solids Characterization

A comparison of the ultimate analysis of solids recovered from the tar samples with that of the respective coals shows that in all cases the tar solids contain greater amounts of nitrogen and sulfur than the coals. Since these solids are coal particles which did not descend through the entire SFBG shaft to the gasification/combustion zone this finding suggests that compounds of carbon, hydrogen, and oxygen are more easily formed in the carbonization zone whereas nitrogen and sulfur linkages are more resistant to cleavage or reaction.

The ash in the solids recovered from tar from Indian Head gasification shows an enrichment on sodium, magnesium, sulfur, and iron when compared with the ash of the feed coal. As-yet unpublished work on the volatilization of ash components in the SFBG gasification/combustion zone has shown that sodium, magnesium, and sulfur are the most volatile of the ash components.

In the case of both lignites, the mole fractions of the principal basic oxides essentially balance those of the silica and sulfur trioxide. The inorganic solids are therefore a mixture of alkali and alkaline earth silicates and sulfates. The ash from the solids recovered from Rosebud tar does not display such a balance. A petrographic classification by the Niggli method (12) shows that free quartz should be present, suggesting that the inorganic solids in this case are a mixture of alkali and alkaline earth sulfates with quartz particles.

#### CONCLUSIONS

The carbon content of the coal plays the most predominant role in determining the relative amounts of compound types in the organic extracts from tar and liquor. An increase in maf carbon will increase the percentage of paraffins and olefins and aromatics in the tar and will increase the percentage of polar compounds in the liquor extract. The polar fraction in the tar extract decreases as maf carbon in the coal increases. The oxygen content of the coal correlates inversely with the amount of organic material extractable from the liquor. Since the carbon content of the coal is of great importance in determining the molecular framework, and since the oxygen is the major contributor to heteroatomic functional groups, these results show that the effluent composition is dependent upon the molecular structure of the coal. Other coal-specific characteristics of the SFBG effluents include the volatility of the tar and the nature of the inorganic materials exiting the gasifier in the raw gas.

Research on the development of detailed relationships between coal composition or structure and effluent composition is continuing. The results of this study indicate the desirability of testing a wide variety of coals in the SFBG to augment the data base on effluent characteristics.

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